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EFFECT OF ANNEALING HISTORY ON FREE VOLUME IN THERMOPLASTICS

JAG J. SINGH AND TERRY L. ST. CLAIR

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NASA
National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665

SUMMARY

Two different types of thermoplastic glassy polymers have been investigated for the effects of thermal annealing on their free volumes. It has been observed that free volumes in glassy polymers decrease asymptotically to a steady level after about four thermal anneals lasting for 24 hours at a temperature about 50°C below their glass transition temperatures. These results indicate that composites incorporating properly annealed thermoplastic matrices may not experience any additional internal stresses due to subsequent thermal excursions experienced while in service.

INTRODUCTION

High temperature thermoplastics are excellent candidates for use in aerospace applications. They have higher tensile strength, absorb less moisture and retain their mechanical properties up to higher temperatures. Graphite fiber-composites using thermoplastic matrices may therefore be expected to have wider applicability than those using epoxy matrices. However, it has been reported(*) that thermoplastics would exhibit higher annealing effects on their free volumes. As a result, it may be expected that composites containing thermoplastics may suffer increasing internal stresses at the fiber-matrix interface as the free volume in the matrix changes due to in-service thermal variations.

In order to assess the general suitability of thermoplastics for graphite-polymer composites, we have studied the water absorption characteristics of two types of thermoplastic polyimide samples as a function of their annealing history. The results are described in the following sections.

SAMPLE PREPARATION

Two thermoplastic polyimide samples were prepared by MITSUI TOATSU Chemicals, Inc. of Japan using processing techniques developed at Langley Research Center(1). Two additional samples containing 5 mole percent of 4,4'-diaminodiphenyl ether were also prepared using the same general procedure. The latter samples were reported to have better processibility and, consequently, better commercial prospects. X-ray diffraction spectra of all samples were measured to determine their level of crystallinity. The first set of samples (LARC-TPI) exhibited a fairly strong degree of crystallinity,

(*) Prof. J. Aklonis, Univ. of South California (Gordon Conference on the Science of Adhesion, 1985; Private Communication).

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but no measurable crystallinity was detected in the second set. All samples were molded in the form of 2" diameter x 0.1" thick discs. The chemical architecture of the two types of samples are illustrated in figure 1.

EXPERIMENTAL PROCEDURE AND RESULTS

The "as received" samples were weighed and then immersed in distilled water at 90°C for an extended period of time. The samples were weighed at 24-hour intervals. They were kept immersed in hot water until their weights stabilized. The samples were then transferred to a vacuum oven at 100°C. Their weights were monitored every 24 hours until they attained a steady state value. Next, the oven temperature was raised to 200°C and maintained at that level for a period of 24 hours(*). After this annealing process, the samples were resaturated with water, desiccated and then subjected to a second annealing cycle. This process was continued for four annealing cycles after which no further changes in sample saturation moisture weights were observed. The results are summarized in Table I.

Table I

Summary of Saturation Moisture Values After Successive Anneal Cycles

No.	Specimen Type	Sat. Moisture (Wt %) Content After Successive Anneal Cycles(*)				
		n = 0	n = 1	n = 2	n = 3	n = 4
1	LARC-TPI	2.205 ± 0.200	2.132 ± 0.137	2.054 ± 0.140	2.017 ± 0.102	2.019 ± 0.098
2	Modified LARC-TPI	2.856 ± 0.030	2.771 ± 0.065	2.707 ± 0.056	2.659 ± 0.041	2.676 ± 0.056

(*)The saturation moisture values are based on dry weights of samples measured after each anneal cycle, following the desiccation process.

Figure 2 shows how the saturation moisture content changes with the annealing process. It is apparent that the saturation moisture content changes rapidly at first and then approaches a steady state value. The data were least squares-fitted to an empirical expression of the following form:

(*)This temperature is about 50°C below the glass transition temperature (T_g) of the test samples.

$$W_n = W_c e^{-\alpha n} + \beta \qquad (1)$$

where W_n = Saturation moisture content after anneal cycle, n

W_c = Characteristic sample constant

α = Decrement coefficient

β = Annealing constant

The values of the decrement coefficient (α) and annealing constant (β) are summarized in Table II.

Table II

Summary of Sample Parameters

Specimen Type	Characteristic Sample Constant (W_c) (Weight %)	Decrement Coeff (α)	Annealing Constant (β) (Weight %)
LARC-TPI	0.196 ± 0.018	0.7242 ± 0.140	2.016 ± 0.102
Modified Polyimide	0.203 ± 0.015	0.703 ± 0.106	2.657 ± 0.041

Finally, the samples were again examined by x-ray diffraction to detect any changes that the annealing process may have produced in their level of crystallinity. No measurable changes in crystallinity were observed in any of the samples.

DISCUSSION

From the results summarized in Tables I and II, it is apparent that the saturation moisture content in the thermoplastic polyimide samples decreases as a function of the anneal cycles. It appears to attain a steady state value after about four anneal cycles.

Since pre- and post-anneal x-ray diffraction studies did not reveal any changes in the degree of crystallinity of either set of samples, it is concluded that any changes in the saturation moisture weights are related to changes in the amorphous regions where water absorption mostly occurs. The

amporphous regions, besides being generally disordered, also contain microvoids which can presumably change as a result of the annealing process. It may therefore be surmised that any changes in the saturation moisture contents of the samples are directly proportional to changes in the volume occupied by the microvoids in them. (The volume occupied by the microvoids in the amorphous regions of the samples equals the free volume in the samples. Water invades this free volume physically when it enters the test samples.)

Paul has recently investigated[2] gas/vapor sorption and transport in glassy polymers. His "Dual Sorption Model" suggests that, for polymers below their glass transition temperatures, the concentration of the sorbed species is given by the following expression:

$$C = k_D p + \frac{C'_H bp}{1 + bp} \qquad (2)$$

where C = Concentration of water vapor in the polymer

k_D = Henry's diffusion constant

p = Water vapor pressure upstream of the sample

C'_H = Vapor absorption capacity

b = Affinity parameter between the polymer and the vapor

The second term in equation 2 follows a Langmuir form and has been attributed to vapor sorption into fixed sites or microvoids. The volume occupied by the microvoids depends on previous thermal and mechanical history of the sample. It has been reported[*] that thermal annealing below T_g reduces the level of vapor sorption in the polymers. This reduction has been attributed primarily to the reduction in the volume of the microvoids.

Thus our results appear to confirm the findings in reference 2, i.e., thermal annealing in glassy polymers reduces their free volume. However, the free volume--according to the present study--appears to reach an asymptotic value beyond which no further reduction in its value is observed. This suggests that after a certain number of anneal cycles, dynamic equilibrium appears to have been reached between the Langmuir and Henry's law populations. After this equilibrium state has been reached, the volume occupied by the microvoids does not seem to change any further.

It has been previously reported[3,4] that positron lifetime measurements in the polymeric targets can provide a <u>direct</u> means of monitoring their free volumes. An attempt was made to measure the positron lifetime spectra in the

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[*] A. H. Chen: Ph.D Dissertation, The University of Texas at Austin (1978). (Data cited in reference 2).

two types of test samples. However, the intensity[*] of the longlife component was found to be too small[3] to permit accurate quantitative measurement of the effects of the small changes in the free volume resulting from thermal annealing of the test sample.

Finally, it should be noted that the saturation moisture content of the modified LARC-TPI sample is larger than that of the unmodified sample. This indicates that the modified specimen is more "porous" and, consequently, easier to process as reported.

CONCLUSIONS

We have investigated the effects of repeated thermal annealing on two types of thermoplastic glassy polymer samples. Thermal annealing was performed for a period of 24 hours at a time at a temperature about 50°C below their glass transition temperatures. Both types of samples exhibited a reduction in their free volumes following thermal annealing cycles. However, the free volumes appear to reach their asymptotic values after about four thermal anneal cycles, presumably due to the establishment of a dynamic equilibrium between the Henry's law and Langmuir populations of water molecules in the test samples. This suggests that composites incorporating thermoplastic matrices which have been appropriately annealed prior to their use may not experience any additional internal stresses at the fiber-matrix interfaces due to thermal excursions experienced later. It is therefore concluded that graphite-composites incorporating properly annealed thermoplastic glassy polymers may be ideal candidates for aerospace applications.

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[*] It is the lifetime and intensity parameters characterizing the longlife components in the positron spectra that reflect the effects of the changes in the molecular environments of the positronium atoms believed to be formed in the free volume cells in the test medium. A change in the free volume would change the degree of overlap between the electron wavefunctions of the Ps-atoms and the surrounding molecular electrons, with a consequent change in the positron annihilation characteristics.

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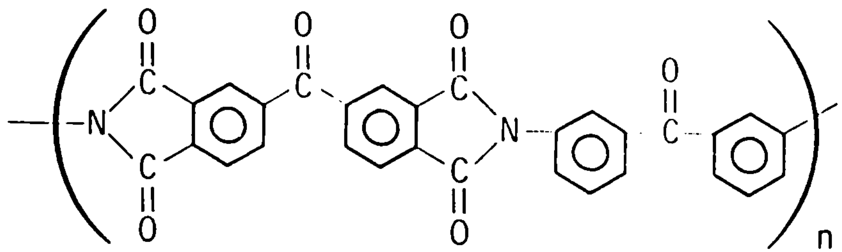
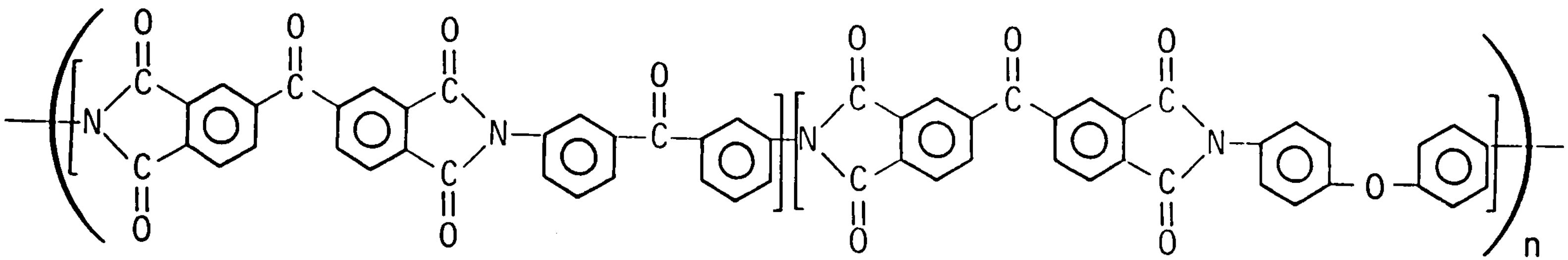


LARC-TPI



Modified LARC-TPI

Figure 1. - Chemical structure of LARC-TPI and Modified LARC-TPI.

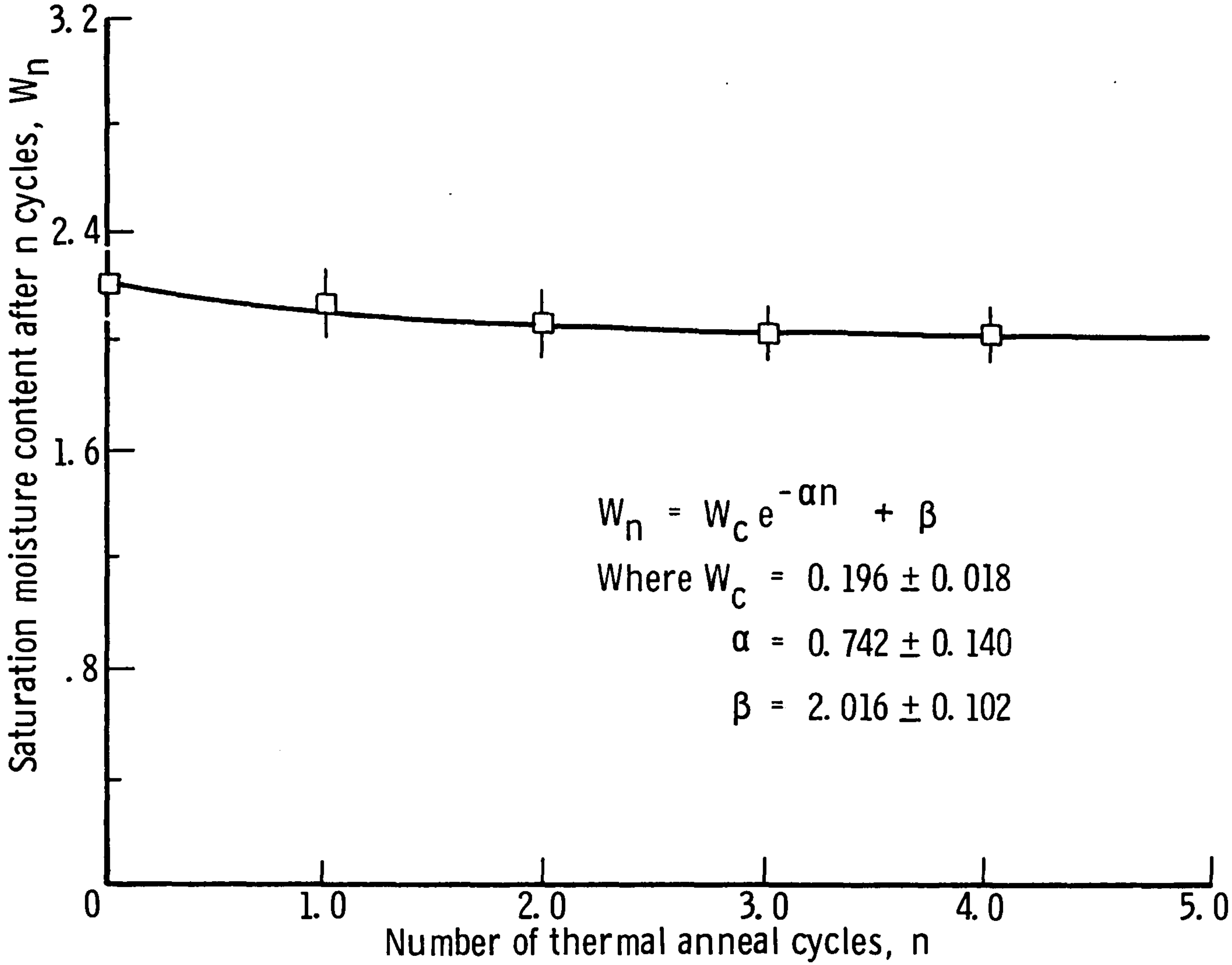


Figure 2(a). - Effect of thermal anneal cycles on saturation moisture content in LARC-TPI samples.

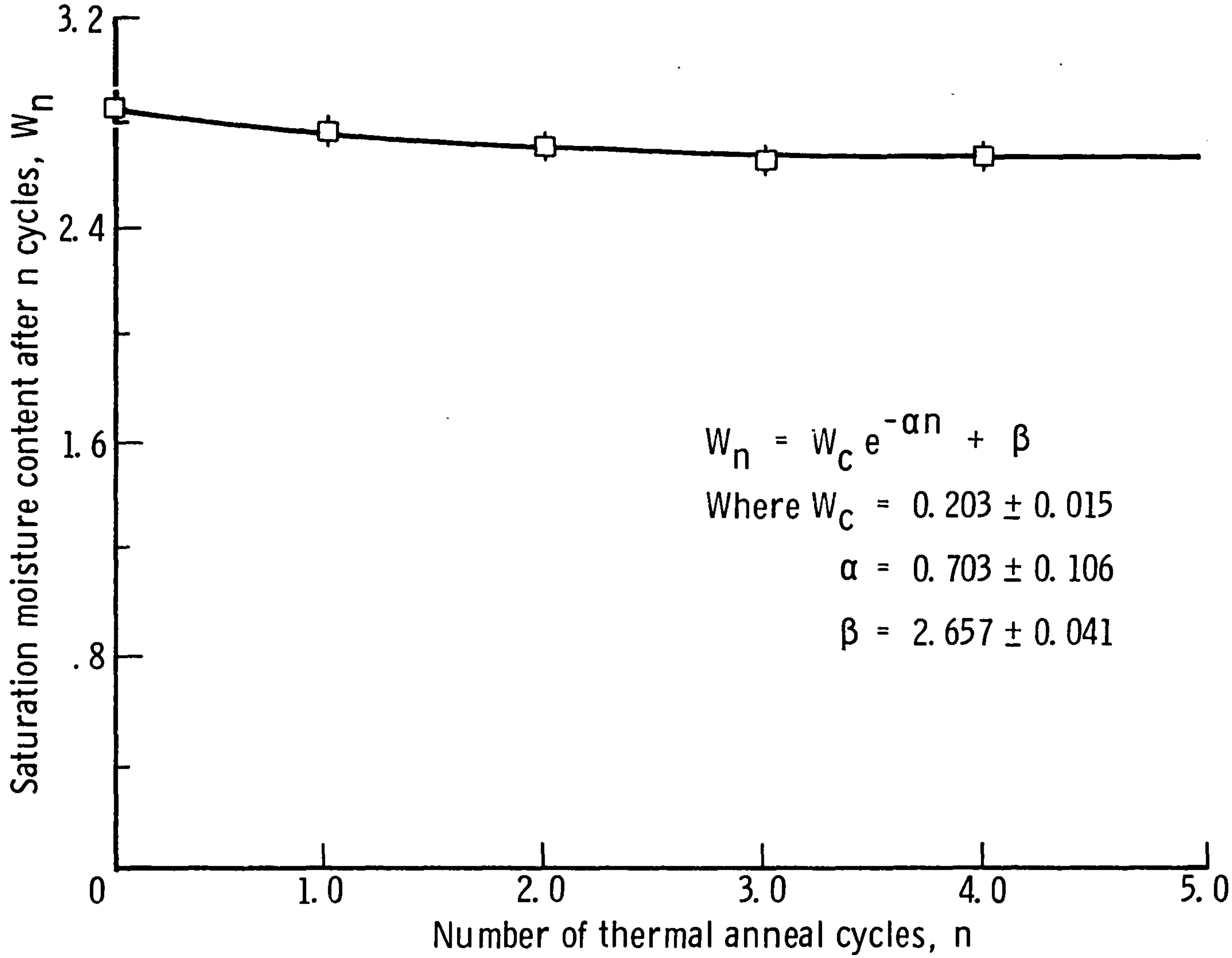


Figure 2(b). - Effect of thermal anneal cycles on saturation moisture content in modified LARC-TPI samples.

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